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Distribution of copper clusters in cobalt-containing nanowires

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A method of application of the nuclear magnetic resonance method to determine the structure of nanowires with the composition $Co_{80}Cu_{20}$ is proposed. Nanowires prepared using templat matrices by electrolytic deposition have been studied. The pore thickness is $10\,\mu$m and the pore diameter is 100 nm. The structure of homogeneous copper and cobalt nanowires was determined by analysing nuclear magnetic resonance data on ^{59}Co in the local field and three-dimensional modelling. Based on the analysis of nuclear magnetic resonance spectra, information about the distribution of hyperfine fields in the investigated nanowires, as well as on the number of cobalt atoms with different types of nearest-neighbour environment was obtained. Based on the data on the number of cobalt atoms in the coordination of which copper atoms are absent, it is established that in these nanowires the crystalline structure of FCC type is realised. Earlier, evaluation and comparison of the intensity of resonance lines showed that clusters with agglomeration of about 30 atoms are formed in the volume of cobalt. Three-dimensional modelling allowed us to clarify the shape of these clusters.Three-dimensional modelling allowed us to clarify the shape of these clusters. On the basis of the analysis of nuclear magnetic resonance spectra and three-dimensional modelling, taking into account the composition of nanowires, conclusions about the structure of homogeneous cobalt-containing nanowires were made.

Keywords: nanowires, nuclear magnetic resonance, modelling, clusters.

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1. Introduction

Information about the structure of low-dimensional systems is necessary for understanding and analyzing the phenomena observed in these systems, however, the studied structural features have atomic scales due to the smallness of objects and their determination is a challenging experimental task. Ferromagnetic cobalt-containing nanowires are nanomaterial which have been actively studied [1–4]. Nanowires are used in magnetic recording devices, spin electronics, and sensors [5]. They are used in microelectromechanical systems [6], magnetically sensitive sensors [7], and data storage devices [8]. The use of nanowires in terahertz radiation systems is also actively studied since it opens up opportunities for creating super-high-speed communication systems [9]. Finally, it is possible to realize the effect of gigantic magnetoresistance in Co/Cu nanowires under certain conditions, and the materials in which this effect is observed are not only of great practical importance, but they also address fundamental issues in the field of spintronics [10].

The matrix synthesis method is one of the relevant methods of nanowire preparation [11–14]. There are two types of matrices used: porous aluminum oxide [15,16] and polymer track membranes [17,18]. The structure of these nanowires is affected by the type of matrix used, the composition of the electrolyte, and the preparation mode [19,20]. It is necessary to use local research methods due to the small size of the studied structural features. The Mossbauer spectroscopy method was used in Ref. [21] to study homogeneous FeNi and FeCo nanowires, which makes it possible to estimate the magnitude of the magnetic field on the nucleus and its change depending on the nucleus-probe coordination. However, this method is not applicable for CoCu nanowires. The nuclear magnetic resonance (NMR) method is another local method, which makes it possible to estimate the distribution of hyperfine fields in nanowires. The NMR method was previously used to study nanowires made of pure cobalt, nanowires with $Co_{85}Cu_{15}$ composition, Co/Cu layered nanowires [18]. This paper shows the effect of electrolyte concentration and copper content in it on the intensity of resonance lines characterizing the type of crystal structure. The impact of the pore diameter in membranes and the presence of organic additives on the type of crystal structure in nanowires was estimated in Ref. [22]. The author of Ref. [23] compared homogeneous nanowires made of pure cobalt and nanowires with $Co_{80}Cu_{20}$ composition. It has been shown that extended shaped copper clusters of about 30 atoms are formed in homogeneous cobalt-containing nanowires with $Co_{80}Cu_{20}$ composition.

However, the question of the structure of nanowires — the nature of the placement of copper clusters in the volume of nanowires — remained open. This paper presents an analysis of NMR spectra and three-dimensional modeling data on an atomic scale for determining the structure of cobalt-containing homogeneous nanowires with $Co_{80}Cu_{20}$ composition.

a *b*

Figure 1. Measuring coil for recording the NMR signal from ^{59}Co nuclei for nanowires: top view (*a*) and side view (*b*).

2. Samples and experimental procedure

Template matrices made of polyethylene terephthalate film were used to prepare nanowires. The thickness of the matrix was $10\,\mu$m, pore diameter was 100 nm, pore density was $1.2 \cdot 10^{-9}$ pores per cm^2. The nanowires were prepared by electrodeposition. A detailed description of the preparation method and the equipment used is provided in Ref. [24].

The nuclear magnetic resonance spectra on ^{59}Co nuclei were recorded in a local field at a liquid helium temperature of 4.2 K. Upgraded SXP 4100 pulse phase-coherent NMR spectrometer („Bruker") was used to record the spectra. NMR spectra were recorded using the frequency sweep method in the frequency range of 250−140 MHz. The spin echo signal was formed by a sequence of two coherent radio frequency (RF) pulses — a solid echo pulse sequence. A flat solenoid measuring coil was fabricated to record the NMR signal from ^{59}Co nuclei (Figure 1).

Square plates with a size of 10×10 mm, cut out of the membrane, were used in the experiment. These plates were placed and centered in the measuring coil of the NMR sensor using quartz spacers. The sequence of RF pulses used created an alternating magnetic field in the coil with the sample with an amplitude of a circular component of approximately 12 Oe. The delay between pulses was $13\,\mu$s with an RF pulse duration of $0.7\,\mu$s. The recording step of the NMR spectrum is 1 MHz. Phase alternation of RF pulses was applied in the pulse sequence in order to reduce the distortion of NMR spectra due to interference effects and transients in the resonant circuit. The measurements were performed at a constant RF pulse amplitude over the entire width of the experimental NMR spectrum.

3. Results and discussion

Let us provide some explanations of what data we extract from experimental nuclear magnetic resonance spectra as part of this study. A local magnetic field is formed on the ^{59}Co nuclei due to the hyperfine interaction. The magnitude and direction of this local magnetic field depend on the structural and magnetic features of the nucleus-probe coordination. The NMR method makes it possible to estimate the distribution of local fields in the studied nanowires. For example, the calculated value of the local field for ^{59}Co atom located in a FCC-type crystal lattice is -22.8 T [25], an experimentally determined value: -21.6 T [25]. The replacement of one cobalt atom for a copper atom in the nucleus-probe coordination results in a decrease of the resonant frequency by approximately 16−18 MHz. The relationship between the magnitude of the local field and the resonant frequency is determined by the gyromagnetic ratio. The dependence of the magnitude of the hyperfine field on the type of coordination is described by the expression:

$$H_{hf} \approx H_{hf}^{b} - \Delta H_{hf}^{1}(n^{b} - n^{1}), \tag{1}$$

where H_{hf}^{b} is the hyperfine field in bulk material, n^{b} is the coordination number in bulk material, shift ΔH_{hf}^{1} ($-1.8 - -1.6$ T [26]), n^{1} is the number of cobalt atoms in the immediate environment.

Figure 2 shows the experimental NMR spectrum and the result of its processing for nanowires with $Co_{80}Cu_{20}$ composition.

The line I_{FCC} in Figure 2 corresponds to cobalt atoms surrounded by cobalt atoms in the FCC crystal structure, the line I_{HCP} corresponds to cobalt atoms in a HCP crystal lattice. The low value of intensity I_{HCP} can be attributed to the joint deposition of cobalt and copper, the latter of which has a FCC structure. The formation of a FCC structure caused by copper has been observed, for example, in superlattices [27]. The lines I_1 (200 MHz), I_2 (182 MHz), I_3 (164 MHz), in accordance with the expression (1), characterize the number of cobalt atoms, in the immediate environment of which there are from one to three copper atoms, respectively. It was shown in Ref. [23] that copper

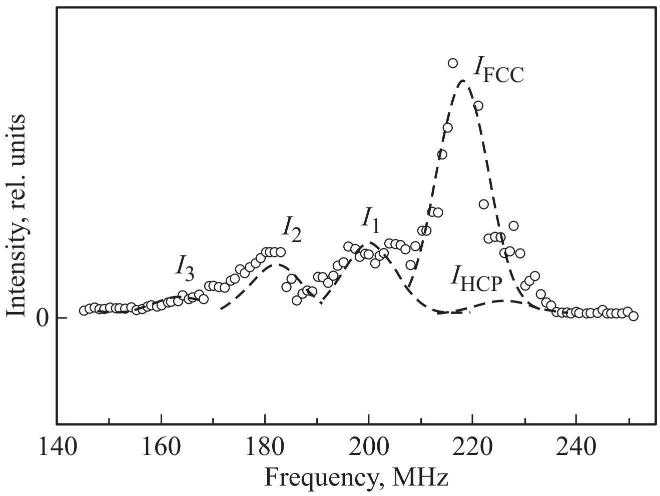

Figure 2. Experimental (circles) and calculated (dotted lines) NMR spectra of nanowires with $Co_{80}Cu_{20}$ composition.

clusters with an extended shape and agglomeration of about 30 atoms are formed in these nanowires. Let us describe the structure of these nanowires using three-dimensional modeling and calculated and experimental NMR data.

There should be 80 cobalt atoms for 20 copper atoms since nanowires have $Co_{80}Cu_{20}$ composition. It is estimated that a cluster agglomeration comprises 28 atoms according to nuclear magnetic resonance data. Therefore, there should be at least 112 cobalt atoms with such a composition of nanowires. Figure 3 shows a three-dimensional model of a copper cluster surrounded by cobalt atoms (Figure 3, *a*) and the calculated NMR spectrum (Figure 3, *b*).

As indicated above, there should be 112 atoms of cobalt for 28 atoms of the copper cluster taking into account $Co_{80}Cu_{20}$ composition. However, only 75 atoms form the shell of the copper cluster, which differs from the nominal composition of the nanowires. The resonance lines I_1-I_4 of the calculated spectrum are in agreement with the experimental data. There are two difficulties at this stage: firstly, there is a discrepancy between the nominal composition of the nanowires and the composition estimated using NMR data, and, secondly, an empirical assessment of the intensity of the resonance line I_{FCC}. Let's estimate how an increase of the cluster size will affect the number and types of coordination of cobalt atoms and, accordingly, the calculated NMR spectrum (Figure 4).

Table 1. The number of cobalt atoms with different types of coordination. Model of a copper cluster of 63 atoms

Number of copper atoms in coordination	Number of Co atoms
1	38
2	32
3	30
4	14
5	4

Figure 4 shows a cluster consisting of 63 copper atoms (black balls), 118 cobalt atoms (gray balls) forming the cluster shell. Table 1 shows the number of cobalt atoms with different coordination.

The calculated NMR spectrum (Figure 4, *b*) shows that the resonance line I_3 has an intensity significantly higher than in the experimental spectrum. This is attributable to the fact that the surface of the cluster increases and a greater number of cobalt atoms with three copper atoms in coordination appear, compared with a cluster with a smaller surface area. In summary, an increase of the cluster size leads to a deviation from the nominal composition and a resonance line of I_3 with excessive intensity is formed.

Let's return to the model of a cluster of 28 copper atoms and build two such clusters. If we assume that each of the

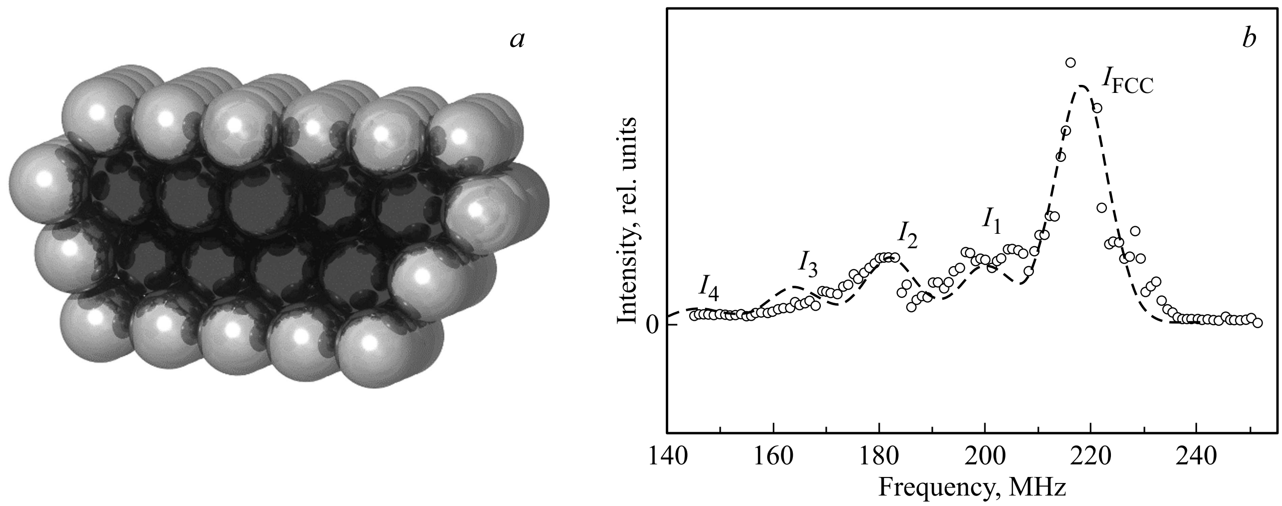

Figure 3. (*a*) A cluster of 28 copper atoms (black balls) surrounded by cobalt atoms (gray balls). The atomic layer is not shown in front of the observer. (*b*) Experimental (circles) and calculated (dotted line) NMR spectra for this structure.

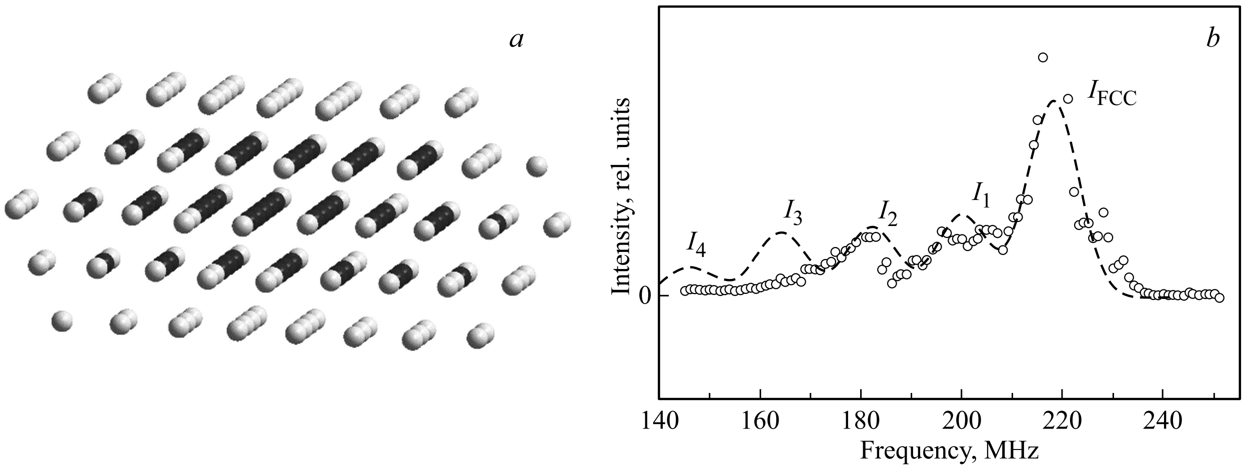

Figure 4. (*a*) A cluster of 63 copper atoms (black balls) surrounded by cobalt atoms (gray balls). (*b*) Experimental (circles) and calculated (dotted line) NMR spectra for a cluster of 63 copper atoms.

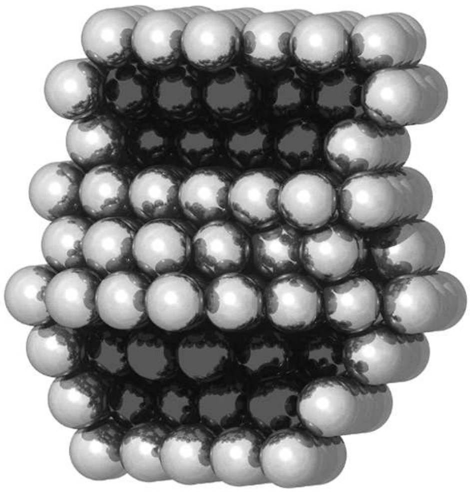

Figure 5. Two clusters of 28 copper atoms each (black balls) surrounded by cobalt atoms (gray balls). The shells of the clusters are separated by a single atomic layer of cobalt. The atomic layer is not shown in front of the observer.

two copper clusters has an individual cobalt shell, then the copper clusters, on average, will be separated by two cobalt atomic layers. There are no cobalt atoms without copper atoms in coordination in this situation and, therefore, the resonance line is I_{FCC}. Since the line I_{FCC} has the highest intensity of all the resonance lines of the NMR spectrum, the macroscopic model should contain cobalt atoms, in the coordination of which there are no copper atoms. The second coordination area is not taken into account in the approach used. Let's place these atoms in the form of an atomic layer separating two clusters (Figure 5).

There are 56 copper atoms (2 clusters of 28 atoms) and 236 cobalt atoms in the model of two copper clusters separated by a single atomic layer of cobalt atoms shown in Figure 5. 156 atoms of these 236 cobalt atoms are in the cluster shells, and 80 atoms are in the atomic layer of cobalt separating these clusters. Table 2 shows the number of cobalt atoms with different coordination.

Table 2. The number of cobalt atoms with different types of coordination. Two clusters of copper of 28 atoms

Number of copper atoms in coordination	Number of Co atoms
0	80
1	48
2	54
3	30
4	12

This structure corresponds to the calculated NMR spectrum shown in Figure 6.

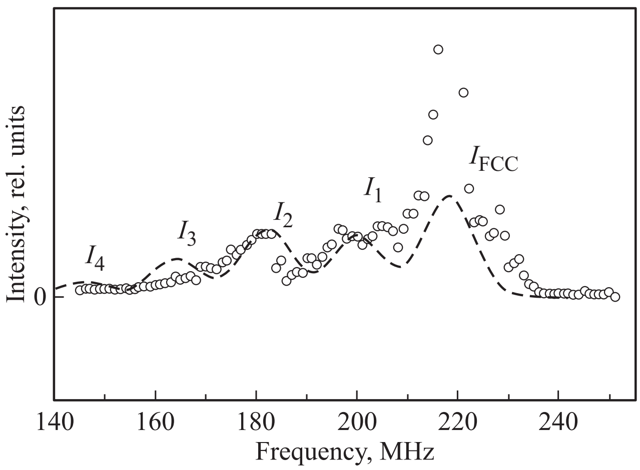

Figure 6. Experimental (circles) and calculated (dotted line) NMR spectra for two clusters of 28 copper atoms surrounded by cobalt atoms and separated by a single atomic layer of cobalt.

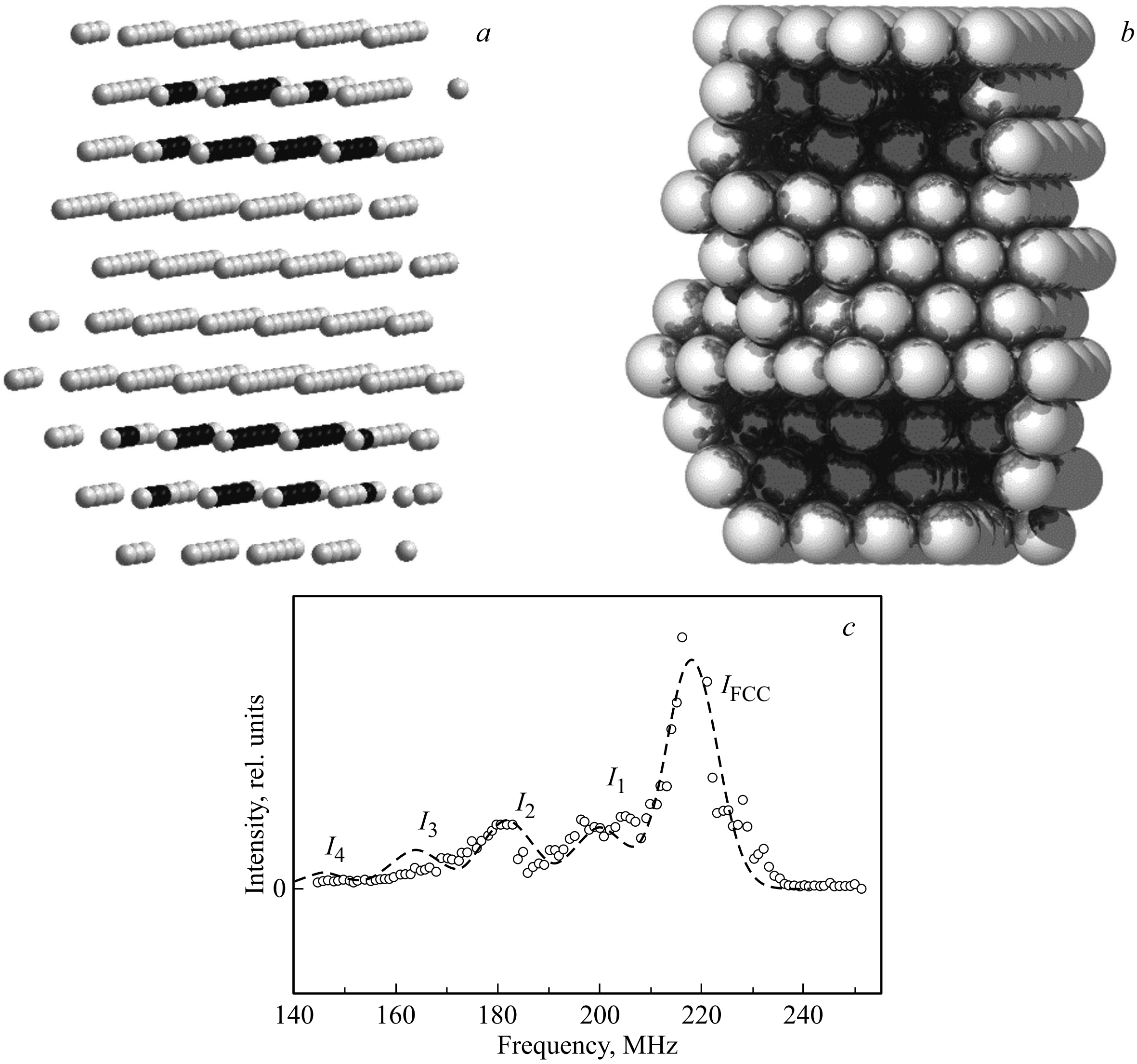

Figure 7. Two clusters of copper (black balls) of 28 atoms with cobalt shells (gray balls) and two atomic layers of cobalt between the clusters (*a*). Visualization of this structure (*b*). Experimental (circles) and calculated (dotted line) NMR spectra of this structure (*c*).

One can see a high level of coincidence for the resonance lines $I_1 - I_4$ in the calculated spectrum shown in Figure 6, but the intensity of line I_{FCC} is too low. Let us increase the thickness of the cobalt layer from one to two atomic layers. A schematic representation of the resulting structure is shown in Figure 7, *a*, visualization — in Figure 7, *b*, calculated NMR spectrum — in Figure 7, *c*.

It can be seen that the calculated spectrum of the proposed model makes it possible to describe the experimental NMR spectrum. The proposed structure consists of 372 atoms including 56 copper atoms, 156 cobalt atoms forming cluster shells, 160 atoms in two atomic layers separating the copper clusters. It should be noted that the presented structure model corresponds to the nanowire composition of $Co_{85}Cu_{15}$. However, this deviation does not seem significant due to the peculiarities of the production technology.

4. Conclusion

At three-dimensional model of the structure of homogeneous nanowires with a nominal composition of $Co_{80}Cu_{20}$ is proposed based on the interpretation of experimental NMR spectra: nanowires consist of clusters of copper with an agglomeration of about 30 atoms. Copper clusters have a shell of cobalt atoms. The cluster shells are separated by two atomic layers of cobalt. The results obtained allow concluding that the studied nanowires have a deviation from the nominal composition: $Co_{85}Cu_{15}$.

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Conflict of interest

The authors declare that they have no conflict of interest.

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